Utilization of high-calcium fly ashes through mineral carbonation: the cases for Greece, Poland and Spain

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ABSTRACT

Limited utilization possibilities of high–calcium fly ashes (HCFA) are a serious issue not only in Europe, but also worldwide. The properties of such waste from coal-fired power plants could be conveniently treated in order to make their compositions compliant with national regulations and allow their use in a variety of industrial applications. This work reports on an investigation of mineral carbonation of HCFA from Greece, Poland and Spain with total CaO contents between 10 and 15 wt.%. Two types of experiments, batch and continuous flow, with and without the addition of water vapor, were performed. Best carbonation efficiency obtained was 47 % of the bulk CaO content. The free lime content of the samples was found to be the controlling factor. After treatment, the amount of free lime was reduced

to values suitable for their utilization as supplementary cementitious materials. The addition of water to the system played also an important role in the progress of the carbonation reactions. Our results strongly suggest that a carbonation treatment of HCFA could contribute to the circular economy of such waste materials and potentially increase their utilization in the construction industry, as well as make a significant contribution to lowering of the CO_2 emissions in coal-burning industrial facilities.

KEYWORDS

Carbon dioxide, industrial waste, gas-solid carbonation, coal fly ash

1. Introduction

Mineral carbonation is one of the safest and environmentally benign technologies for Carbon Capture and Storage. This mechanism consists of the fixation of carbon dioxide into calcium and/or magnesium bearing minerals to form stable carbonates. Recent interest on such mechanism has focused on the use of natural rocks [1–3] and industrial wastes [4–6] as suitable materials for mineral carbonation. Among the latter, high–calcium fly ashes (HCFA) from coal burning power plants, with CaO contents between about 10 and 50 weight %, have been proven to have a high mineral carbonation potential [7]. CO_2 mineralization through direct carbonation is associated with valorization of waste materials, i.e. HCFA, which can be used as supplementary cementitious materials. CO_2 and fly ash valorization through mineral carbonation has significant potential for sustainable carbon cycle towards circular economy [8].

Total world production of fly ash every year is estimated to be at least 675 Mt with the average utilization factor equal to 16% [9,10]. European Coal Combustion Products Association statistics from 2016 states that the fly ash production in Europe reached 145 Mt with a 20.1% utilization rate. Among these, only 20% of HCFA are being utilized due to the existing regulatory frameworks considering the use of fly ashes in Europe [11]. Calcareous (CaO < 10 wt.%) fly ashes can be used in the European Union

under regulation EN 450 – 1 [12]. HCFA utilization is restricted to blended cements when complying with EN 197 [13].

Generation of HCFA is generally associated with the burning of lignite coal, being Greece, Poland, and Spain among the main producers of this kind of waste in the European Union [14]. In Greece, where 12 Mt of fly ash come from lignite combustion, the state established the 'Hellenic Specification for the Use of High Calcium Fly Ashes in unreinforced concrete or cement products' [11]. Fly ash is used mainly to replace clinker and it is believed that a better utilization strategy should be developed because of the low fly ash processing rate [15]. Poland, in addition to the standard use of calcareous fly ash in concrete, adopted the PN–S–96035:1997 regarding the utilization of fly ash in road construction and BS EN 14227-4 for hydraulically bonded mixtures [16]. Around 60% of the total Polish fly ash production is currently utilized [17]. Additional regulations exist in Spain including 'UNE83420 – Cement Additions – Fly Ash Specifications for Fly Ashes with CaO content in excess of 10%' [18,19].

Factors affecting the fly ash composition include the type of the fuel used in the combustion process, as well as ash separators and collection system technologies [20,21], leading to a significant variability. Restrictions introduced by governments regarding the addition of HCFA to cement are based on limiting the content of free lime present in construction materials, that may eventually lead to durability problems due to delayed hydration and subsequent expansion and cracking [22].

Previous work on the evaluation of the properties of cement pastes with addition of raw [23,24] and carbonated HCFA [25,26] suggests that the latter may have a positive (or, at least, not detrimental) long term effect on the mechanical strength of the concrete. Recently, some investigations have been conducted regarding carbonation of HCFA [27–29]. Successful carbonation has been reported previously with a fly ash with 35wt.% CaO content [7]. Furthermore, Pei et al. [25] estimated that addition of 5% of carbonated fly ash to the cement would result in savings of about 1.96 USD per ton of cement produced.

The work presented in this paper is aimed to characterize the carbonation of HCFA from Greece, Spain and Poland with calcium contents between 10 and 15 CaO wt.%. A comparison of the carbonation

efficiencies of fly ashes with similar CaO contents has been carried out in order to give insights on such processes and their utilization as part of CO_2 capture strategies [30].

2. Materials and methods

2.1 Material characterization procedures

Three different fly ashes were chosen with bulk contents of CaO between ~10 and 15 wt.%, as shown in Tab. 1. The Megalopolis fly ash is a waste material produced at the Megalopolis Power Plant in Arcadia, Greece. It burns lignite and black coal, with a total power capacity of 850 MW. The Belchatow sample is a fly ash derived from the power plant of the same name in Poland with a 5298 MW installed power. It has 13 electric blocks and flow-dust boilers. Fly ash from La Pereda (Spain) comes from the La Pereda Thermal Power Plant located in Asturias, Spain. It is a co-fired power plant with a power capacity of 50 MW where fuel coal, cob gas and biomass are used. Increased content of CaO in the fly ash is due to the post-combustion capture technology used on site, where lime acts as adsorber for the CO_2 and some residues of it are mixed with the fly ash [31].

Bulk chemical compositions were determined by X-ray fluorescence spectroscopy (XRF) by the fusion bead method on a UniQuant® apparatus from Thermo Fisher Scientific™. Before the experiment, samples were calcined for 2 hours at 1000ºC. Free lime determination tests were performed following the procedures described in [32]. For each test, 1 g of sample was mixed with 50 mL of ethylene glycol and placed in a water bath at 60 ^{0}C for 30 min. Following that, sample was filtered and the filtrate was titrated with a HCl solution (0.1 N) with 2-3 drops of Brome-cresol green solution to the point when it changed color from blue to green. The free CaO content is calculated following the expression:

$$Free\ CaO\ (\%) = \frac{mL\ HCl\ x\ \ normality\ of\ HCl}{10\ x\ sample\ weight}\ x\ 28 \qquad (1)$$

Sample mineralogy was determined by powder diffraction (XRD) using a Bruker D8™ diffractometer, supplied with a theta-theta goniometer. Analyses were conducted in a 2θ deg range of 15 to 70°, with a step-size of 0.02° and measuring time of 1 second per step. Thermogravimetric analysis (TGA) was performed on a TA instruments G50™ machine. Each 30-35 mg sample was heated up from room temperature to 950 ^{0}C with a heating rate of 10 ^{0}C/min under a nitrogen atmosphere with a flow of 60 mL/min. Scanning Electron Microscopy (SEM) was conducted with an Oxford Instruments microscope Zeiss Neon40^{TM}, operated at 15 keV. Infrared transmission spectra were recorded with a FTIR Nicolet 6700™. The samples (~3% total mass) were mixed with KBr (~97%) and pressed into pellets. The analyzed spectra range from 225 cm^{-1} to 4000 cm^{-1}, using 64 scans and 4 data point spacing.

2.2 Chemical and mineralogical composition

Chemical compositions of the studied samples are listed in Table 1. Despite their similar bulk CaO, free lime contents in untreated fly ashes were found to be quite different: 1.96, 0.33 and 4.16 for Megalopolis, Belchatow and La Pereda, respectively (Fig. 1). This is relevant, as CaO not combined with other elements is more accessible for reaction with CO_2. Free lime determination was also performed on the samples with best CO_2 sequestration efficiency. Lowering the free CaO content through carbonation opens new utilization possibilities for the incorporation of HCFA in the production of concrete materials. The free lime content of the samples after carbonation is, in all instances, below 1.5%. This means that most part of the free CaO has carbonated and transformed to calcium carbonate. [12].

Table 1. X-ray fluorescence analyses of the tested fly ashes.

Figure 1. Results of the determination of free lime contents for untreated (solid) and carbonated samples.

The main mineral phases identified include quartz and aluminosilicates (mullite). Lime, anhydrite and gehlenite were also identified in all three samples. The original material of the fly ash from La Pereda

contains some calcite ($CaCO_3$), strongly suggesting some degree of pre-carbonation. On the other hand, anorthite has only been detected in the samples from Megalopolis and Belchatow (Fig. 2).

Figure 2. XRD analysis of fly ashes before and after CO_2 treatment (160 ^{0}C, 8 bars CO_2/CO_2+H_2O, 4 hours). a) La Pereda, b) Megalopolis, and c) Belchatow fly ash. Q – quartz, C – calcite, P – portlandite, A- anhydrite, G – gehlenite, L – lime, M- mullite, An – anorthite.

The pre-treatment carbonation level of the samples was determined by thermogravimetric analysis (TGA). TGA results of untreated fly ash samples are shown in Figure 3. From these data, the initial carbonation degree of the samples was calculated based on the mass loss related to calcium carbonate decomposition at 650 – 950^{0}C. The TGA analysis of La Pereda confirms the presence of minor portlandite. This fly ash has a significant amount of initial natural carbonation, which is equal to 29.5% of its capacity to store CO_2; the Megalopolis and Belchatow precarbonation values are of 8.9 and 0.3%, respectively.

Figure 3. TGA analysis of the fly ash samples.

The SEM study revealed that the Belchatow and Megalopolis samples are mainly composed of cenospheres [33] (round-shaped particles of aluminosilicate glass and quartz), of sizes between 30 and 40 μm. These can be either closed, open, attached to each other or in the case of the larger ones, they may appear filled with smaller cenospheres inside. On the other hand, fly ashes from La Pereda form irregularly-shaped agglomerates of sizes of 2 to 6 μm. (Fig. 4). Both untreated and treated samples were studied in order to assess their microstructural changes upon carbonation. Carbonated samples show a variety of morphologies of the calcium carbonate crystals, which can be attributed to different processing conditions [34]. In the case of La Pereda, fully grown rhombohedral calcite crystals have been observed in the samples treated under closed system and moist conditions, similar to [35–37]. However, changes

experienced upon carbonation of the Megalopolis fly ash resulted in irregularly shaped carbonate particles and small needles [38].

Figure 4. Representative SEM images of untreated (left) and treated – batch reactor with addition of water vapor (right) fly ashes from La Pereda (a), Megalopolis (b) and Belchatow (c).

2.3 Carbonation experiments

Following previous studies [7], carbonation experiments were conducted at 160 ^{o}C for 4 hours on a purpose-designed apparatus. For each ~2g sample, experiments were carried out in pressurized continuous flow (open system) and batch reactors. The open system consists on a stainless steel reactor located inside a furnace with regulated pure CO_2 and N_2 fluxes. Pressure was controlled by pressure reducers and a back-pressure regulator. Water vapor was added by flowing CO_2 (20 mL/min) through a heated stainless steel bubbler, located outside the furnace, prior to entering the reactor system. Thus, a constant gas mixture of pCO_2/pH_2O of 1.5 was achieved. Experiments were carried out at 8 bars of CO_2 + 1 bar atmospheric pressure. Nitrogen was used as a carrier gas for heating and cooling ramps. For the batch reactor (closed system), the same amount of CO_2 was loaded into the reactor prior to heating. After sealing, a final pressure of 10 bar was achieved.

3. Results and discussion

3.1 Continuous pressure flow experiments

X-ray diffraction analysis of the untreated and carbonated samples under continuous flow pressure conditions are shown in Figure 2. For all fly ash types, the differences between untreated and dry carbonated samples are negligible. Belchatow and Megalopolis fly ashes do not show any appreciable calcium carbonate (Fig 2b and 2c). In the case of La Pereda fly ash, indication of calcite is detectable (Fig 2a).

The results of XRD analysis are supported by the FTIR results (Figure 5). One of the most characteristic absorption bands (1100 cm^{-1}) appearing in all fly ashes corresponds to the Si—O stretching vibration, indicating the presence of quartz [34]. The characteristic absorption band peaks for calcite are located at 1418-1423 cm^{-1}, 870 cm^{-1} and 1795 cm^{-1} [35,36]. Again, untreated samples and those carbonated under dry conditions and open flow system show no significant differences, although incipient carbonation of the La Pereda fly ash seems to occur, as suggested by the increase of the intensity of peaks located at 1444 cm^{-1} and 875^{-1} cm (Fig. 5a).

In the case of samples treated with steam in the continuous flow reactor, analyses show clear evidence of carbonation, as calcite appears in the X-ray diffractograms of the treated samples (Figure 2). It is a proven fact that the addition of water vapor accelerates the carbonation process [28,37,38]. Also, lime present in the untreated samples (at 2θ values of 37 and 54 degrees) disappears after treatment, strongly suggesting conversion of lime to carbonates. Furthermore, FTIR analyses confirm the presence of calcium carbonate, evidenced by a noticeable increase of the absorption bands intensity at 1418-1423 cm^{-1} and 867-873 cm^{-1} (Fig. 5). La Pereda and Belchatow samples display an additional absorption band at 1793 – 1799 cm^{-1}, which can also be interpreted as the presence of calcite [36].

Figure 5. Results of FTIR analysis for carbonated fly ash samples (160 °C, 8 bars CO_2/CO_2+H_2O, 4 hours). a) La Pereda, b) Megalopolis, c) Belchatow.

3.2 Batch reactor experiments

Carbonates were observed to form after carbonation in a batch reactor under dry conditions. XRD and FTIR results of the treated samples of La Pereda, Megalopolis and Belchatow reveal the presence of calcite peaks (Figs.2 and 5). Similar to previous studies [7], newly formed calcium carbonates appear after reaction in dry conditions, in agreement with thermodynamic calculations, confirming the feasibility of dry gas-solid carbonation of reactive waste materials [3,39]. Batch reactors have the advantage over

continuous flow reactors of more easily achieving a pressure increase due to heating inside the closed system using the same amount of loaded gas, thus enhancing reaction kinetics [40].

Analyses of samples carbonated in the batch reactor with steam reveal that carbonation process also takes place under the conditions reported above. All XRD data show evidence of calcite and no lime peaks have been identified (Fig. 2). Absorption bands of samples carbonated under these conditions are characterized by peaks at ~1420 cm^{-1}, ~870 cm^{-1} and ~1795 cm^{-1}, confirming the presence of carbonates (Fig. 5). The presence of water is then confirmed to accelerate the carbonation reaction, in agreement with [38,41,42].

3.3 TGA Analysis

The extent of the carbonation reaction is more easily followed from the results of TGA analysis of the treated samples (Figure 6). The first mass loss observed at 135ºC is probably due to gypsum decomposition. This mineral is probably the result of hydration of precursor anhydrite [43], as identified in the XRD patterns, and is clearly observed in the Megalopolis and Belchatow fly ashes after moist treatments (Fig. 6b and 6c). The next mass loss peak, starting at ~400ºC is interpreted as decomposition of portlandite [44], which is observed as a minor component (~0.2 wt.% of the total mass) of the fly ash from La Pereda (Fig. 6a). Portlandite seems to prevail, in such low amounts, even after treatment under open system conditions. This can be interpreted on the basis of observations reported by Montes-Hernandez et al. [45], suggesting that lime is more reactive with CO_2 than $Ca(OH)_2$.

Carbonate species have been observed to undergo decomposition in the ranges of 600-700 and 750-900 ºC, probably indicating the presence of at least two carbonate species with different thermal stability properties. Previous research has stated that anhydrous calcium-based carbonates decompose at different temperatures depending on their crystallinity and their crystal size [46].

Figure 6. Results of TGA analysis for the treated samples: a) La Pereda fly ash, b) Megalopolis fly ash, c) Belchatow fly ash.

The total mass loss due to carbonate decomposition in La Pereda samples ranges between 3.5% (untreated) and 10% (carbonated). In the Megalopolis and Belchatow fly ashes, TGA analyses of the treated materials revealed mass losses of 6.5% and 3.5% in the temperature range between 600 and 950^{0}C. On the other hand, the single decomposition peak observed at 700 ºC in the Belchatow fly ash suggests that only one carbonate phase exists in this sample, unlike in La Pereda and Megalopolis.

3.4 Carbonation efficiency and CO_2 sequestration capacity

The maximum theoretical capacities for CO_2 capture, i.e. assuming all Ca-bearing minerals can eventually carbonate, were calculated from XRF results (Tab.1) and TGA analyses, yielding values of 103.1 (Megalopolis), 120.5 (Belchatow) and 81.2 (La Pereda), all expressed in g of CO_2 per kg of fly ash.

Calculations were carried out following the expression [35,47]:

$$CO_2[wt\%] = \frac{\Delta m_{CO2}[g]}{m_{105^oC}[g]}\, x\, 100 \qquad (1)$$

Where:

CO_2 (wt%) – CO_2 content in the original sample,

m_{105^oC} [g] – dry weight of the sample at 105^{0}C,

Δm_{CO2} [g] – weight loss due to the calcium carbonate decomposition.

The CO_2 contents in the carbonated samples were calculated extracting the CO_2 content in the original sample. The carbonation conversion of the fly ash (ζCaO) is determined by Eq.2:

$$\zeta CaO[\%] = \frac{\frac{CO2(\%)}{100 - CO2(\%)} \times \frac{1}{MW_{CO2}}}{Ca_{total}/MW_{Ca}} = \frac{\frac{CO2(\%)}{100 - CO2(\%)} \times \frac{1}{MW_{CO2}}}{CaO_{total}/MW_{CaO}} \quad (2)$$

Where:

MW_{CO2} - molecular weight of the CO_2 (g/mol)

MW_{Ca}, MW_{CaO} – molecular weights of the Ca and CaO (g/mol)

Ca_{total}, CaO_{total} – percent weight fraction determined by the XRF

Figure 7. Calculated values of the sequestration capacity (g CO_2/kg fly ash) and carbonation efficiency (ζ[%]) of the samples.

Calculated values of the sequestration capacity and carbonation efficiency of the samples are shown in Figure 7. Carbonation efficiency takes into account the calcium in all Ca-bearing minerals of the fly ashes (i.e. anhydrite, free lime, portandite and Ca-silicates). The highest sequestration capacity achieved for La Pereda fly ash was 46.7 %, corresponding to 53 g of CO_2 utilized per 1 kg of fly ash. This result was achieved in the steamed batch experiments. The highest efficiencies calculated for the Megalopolis and Belchatow fly ashes were, respectively, 22.4% and 10.5%, both under open flow system and steam conditions. This can be interpreted as a significantly lower extent of carbonation of the Megalopolis and Belchatow samples, despite their similar CaO contents, strongly suggesting that the presence of free lime plays a key role on the carbonation of such types of materials. Although higher contents of CaO are commonly associated with higher free lime contents, other Ca-bearing minerals commonly present in fly ashes also contribute to the bulk CaO concentration, but their reactivity with CO_2 is much lower than that of free lime, leading to lower CO_2 sequestration capacities and efficiencies. The values calculated in this work are higher than those previously reported [48–50].

4. Conclusions

This study provides a comparison of the carbonation potential of different European fly ashes with similar CaO contents (10-15%) in order to shed light on the compositional constraints that control reaction of CO_2 with these materials in view of their utilization as addition to cementitious materials. La Pereda fly ash achieved the best carbonation efficiency (46.7%) among the studies samples, corresponding to 53 g of CO_2 per kg of fly ash. These results are similar to the values obtained by [7], where carbonation of a 35% CaO HCFA lead to 48% carbonation efficiency (117 g of CO_2 per kg of fly ash sequestration capacity). The high carbonation potential of La Pereda sample, despite its lower bulk CaO, is due to the fact that free lime is the predominant Ca-bearing mineral. Direct HCFA carbonation at low pressures and temperatures seems to be a promising technology for CO_2 sequestration, even for materials with relatively low CaO. In order to implement this process in industry, carbonation experiments with diluted CO_2 simulating power plant flue gas should be performed to investigate its feasibility. HCFA carbonation with flue gas instead of pure CO_2 would significantly reduce the cost of such process [51].

Two different experimental systems were compared: batch and continuous flow, both with and without addition of steam. The batch moist treatment has shown to achieve the highest carbonation efficiency.

Free lime determination tests revealed that the carbonation reaction led to almost complete conversion of free CaO into calcium carbonate, for all types of fly ashes. Considering the present EU regulations regarding fly ash admixtures for concretes (EU 450 – 1), lowering this value below 1.5% could be a starting argument for implementing carbonation processes similar to the ones described in this paper at coal power plants, as they have the potential to lower their CO_2 emissions and allow the use the carbonated fly ashes in the construction industry. Integrated approach to combine CO_2 utilization with alkaline waste valorization fits within the circular economy concept as it can be simultaneously achieved.

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Table 1. X-ray fluorescence analyses of the tested fly ashes.

Weight %	La Pereda	Megalopolis	Belchatow
SiO_2	46.68	50.72	37.22
CaO	10.33	13.12	15.34
Al_2O_3	22.72	17.66	13.14
MgO	1.33	2.51	0.85
Na_2O	0.72	1.85	0.93
SO_3	4.69	2.61	2.93
K_2O	3.33	1.81	0.20
Fe_2O_3	6.51	8.14	4.99
TiO_2	0.97	0.88	1.59
P_2O_5	0.09	0.22	0.45
SrO	-	0.11	-

Figure 1. Results of the determination of free lime contents for untreated (solid) and carbonated samples.

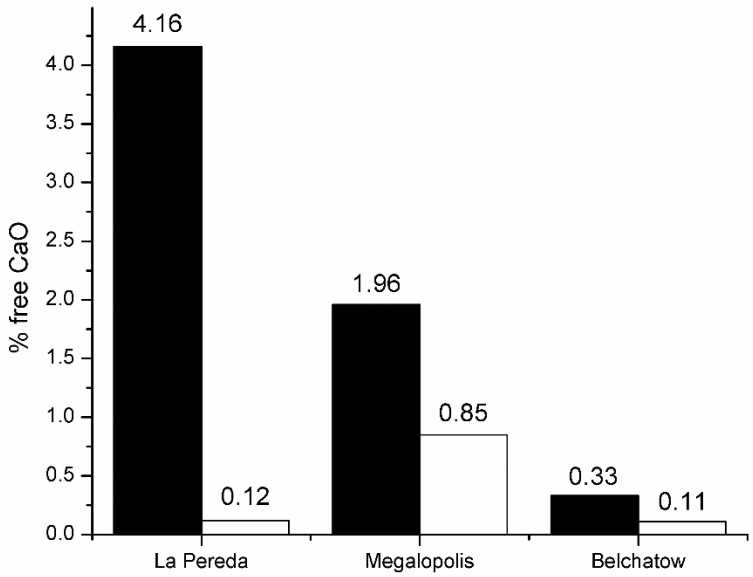
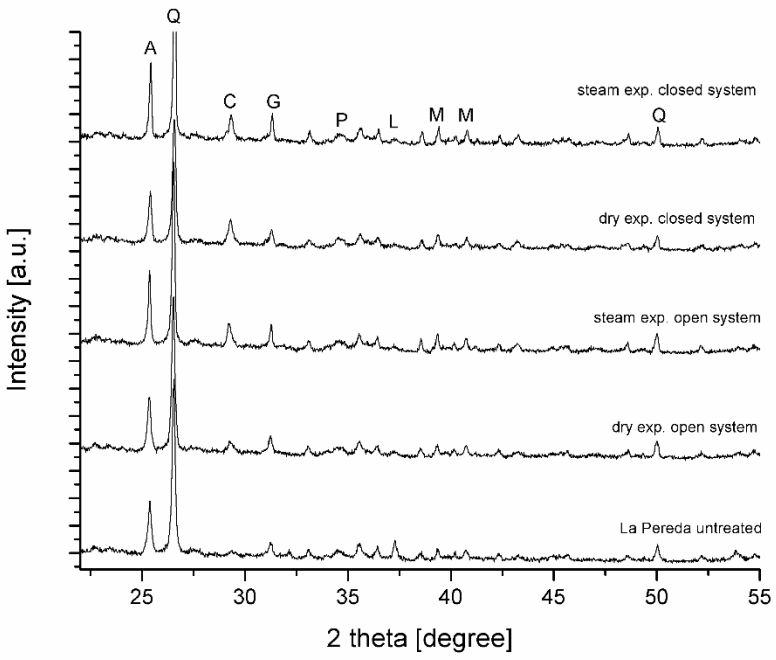
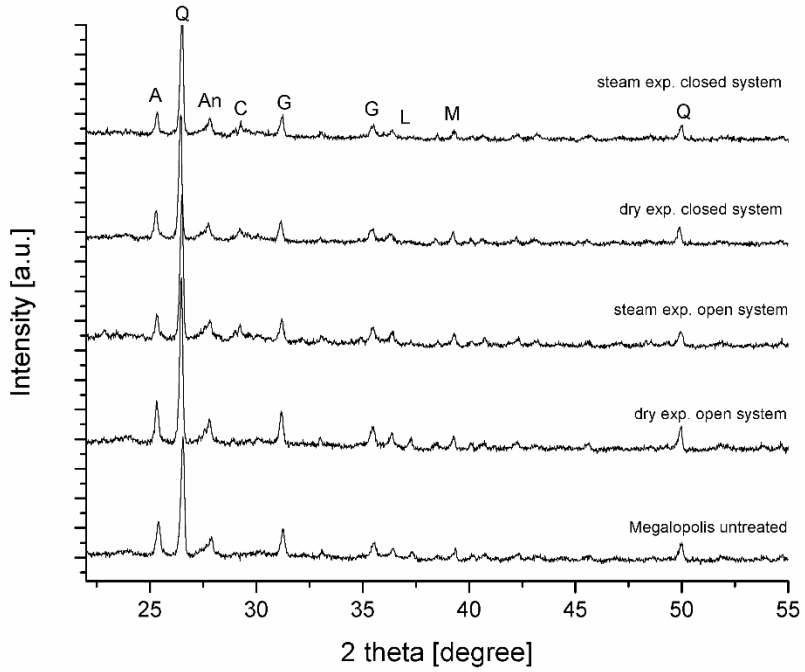


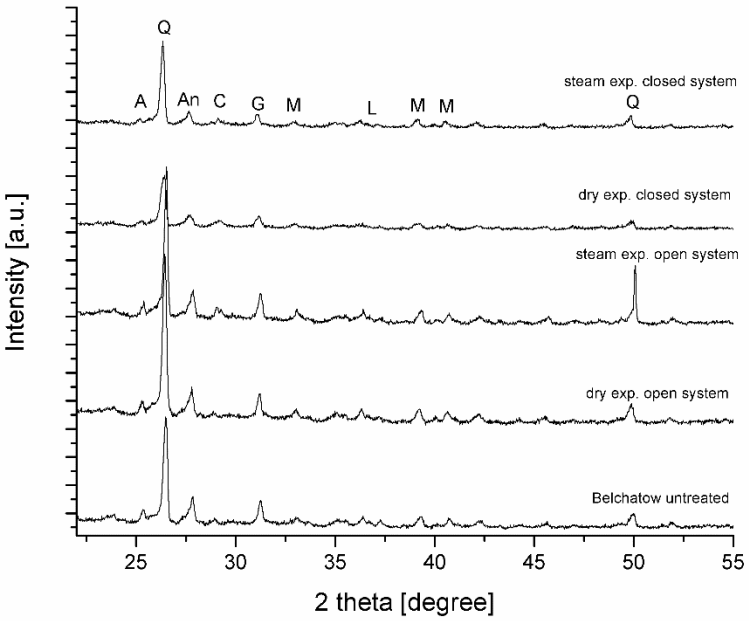
Figure 2. XRD analysis of fly ashes before and after CO_2 treatment (160 ^{0}C, 8 bars CO_2/CO_2+H_2O, 4 hours). a) La Pereda, b) Megalopolis, and c) Belchatow fly ash. Q – quartz, C – calcite, P – portlandite, A- anhydrite, G – gehlenite, L – lime, M- mullite, An – anorthite.



a)


Q
A
An
C
G
G
L
M
Q
steam exp. closed system
dry exp. closed system
steam exp. open system
dry exp. open system
Megalopolis untreated
Intensity [a.u.]
25
30
35
40
45
50
55
2 theta [degree]

b)



c)

Figure 3. TGA analysis of the fly ash samples.

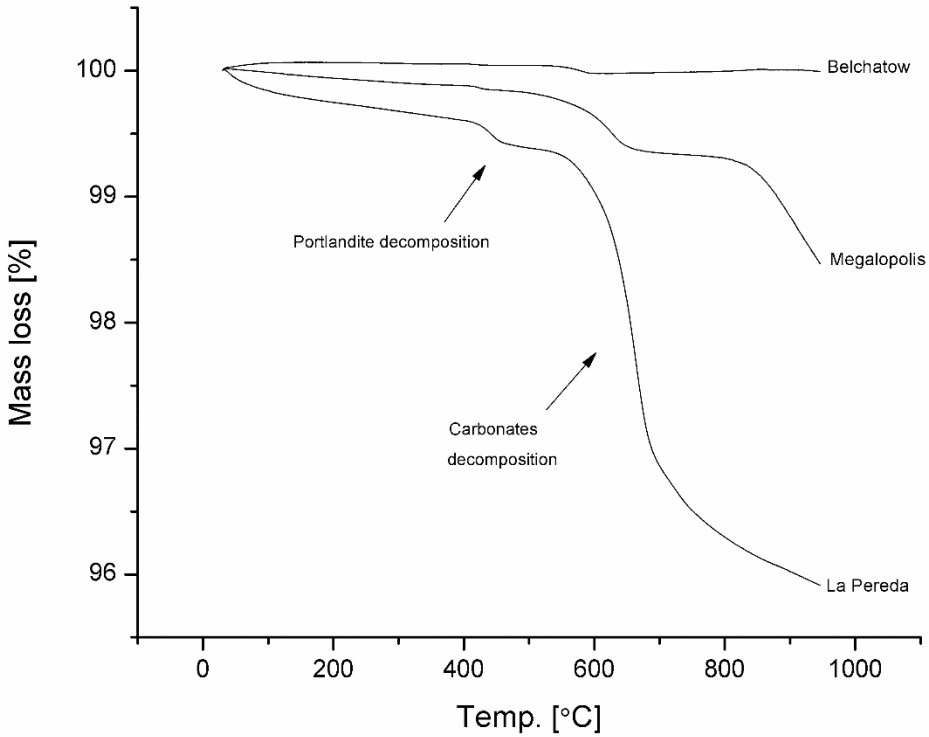
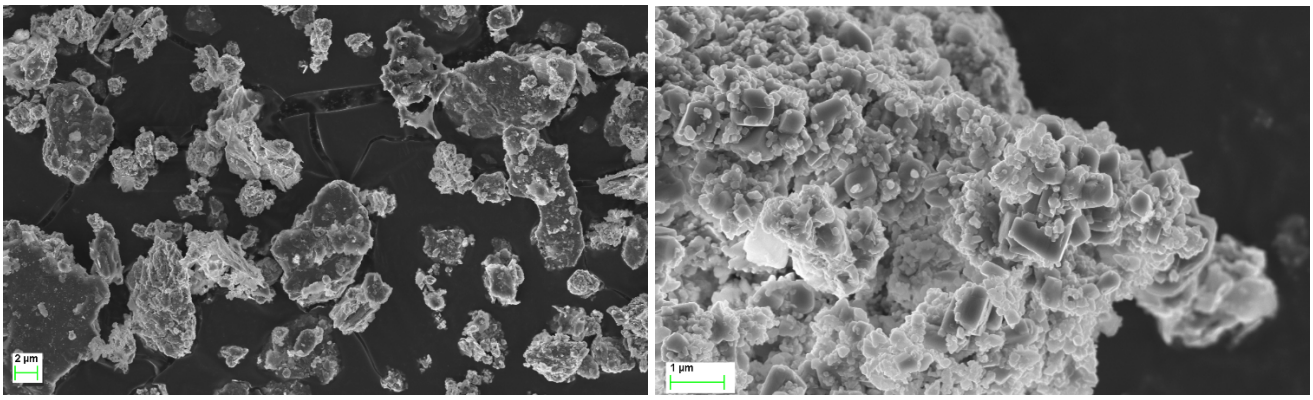
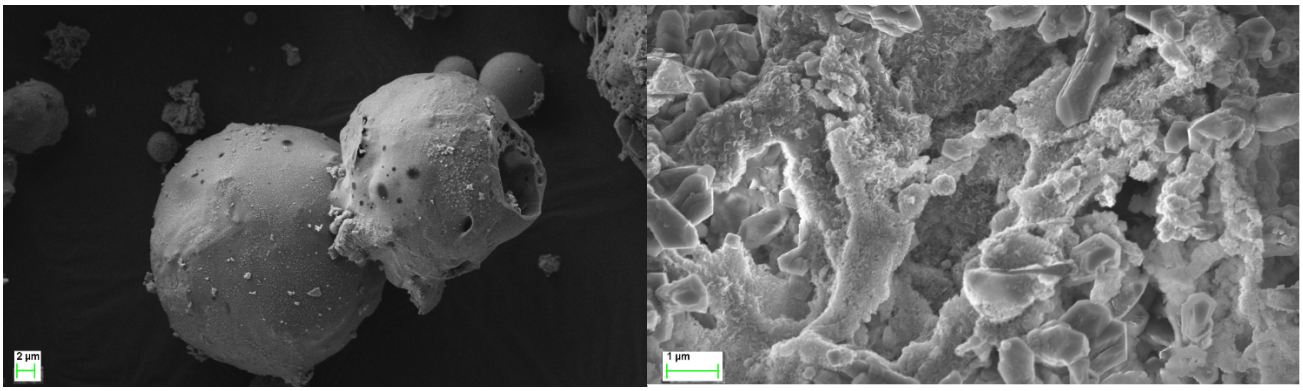


Figure 4. Representative SEM images of untreated (left) and treated – batch reactor with addition of water vapor (right) fly ashes from La Pereda (a), Megalopolis (b) and Belchatow (c).

a)



b)



c)

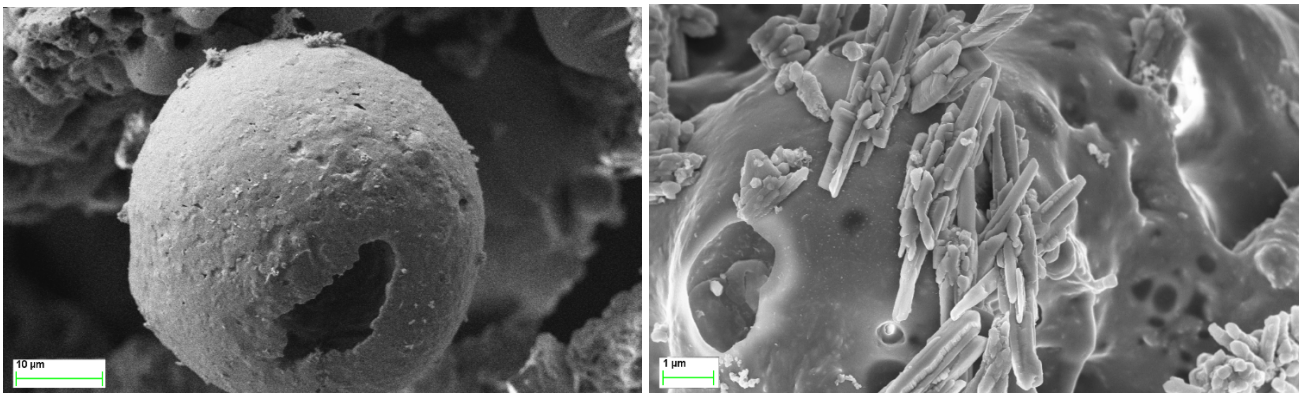
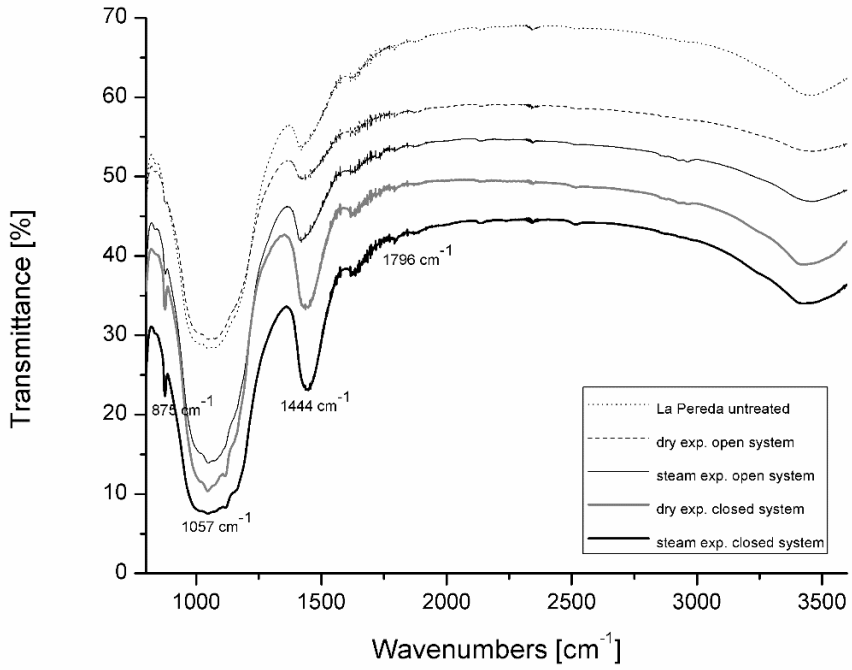
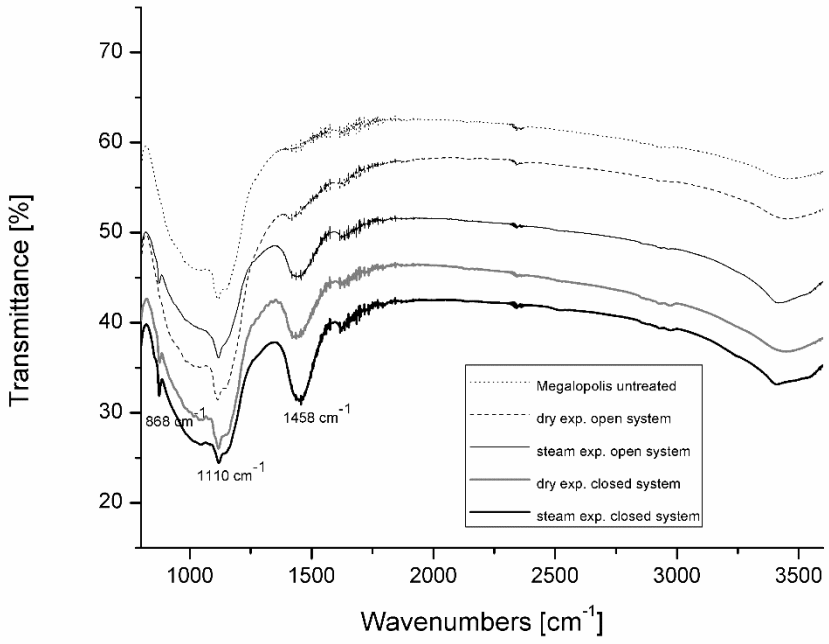


Figure 5. Results of FTIR analysis for carbonated fly ash samples (160 ^{o}C, 8 bars CO_2/CO_2+H_2O, 4 hours).

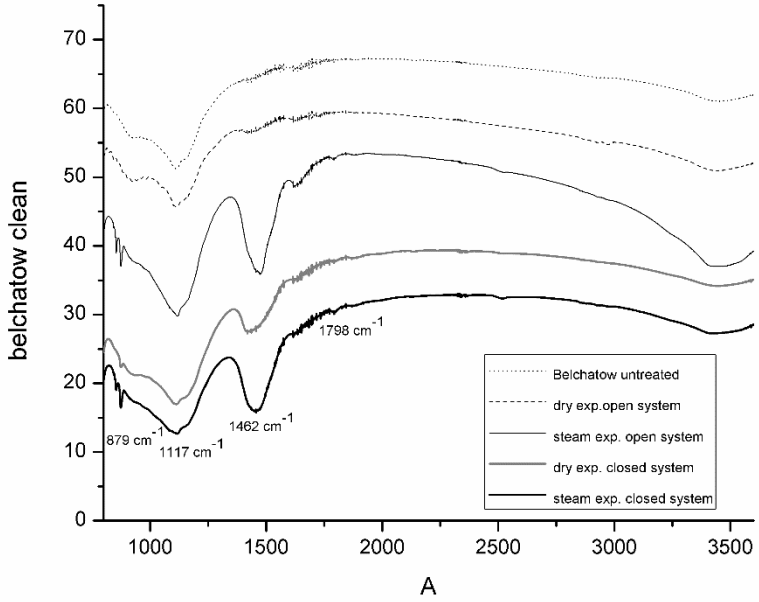
a) La Pereda, b) Megalopolis, c) Belchatow.



a)

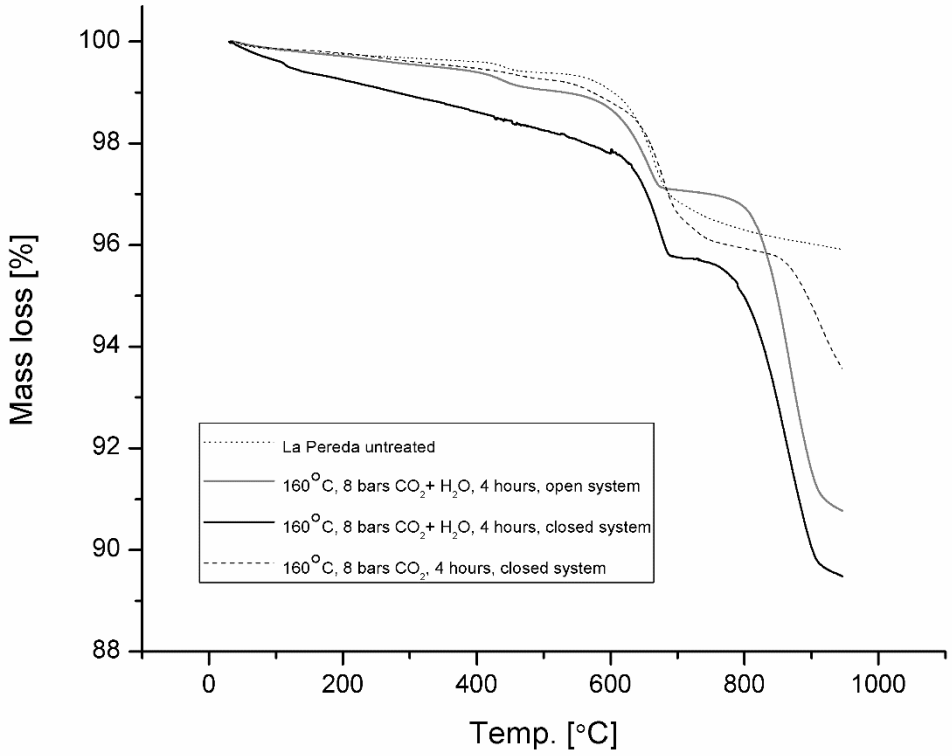


b)

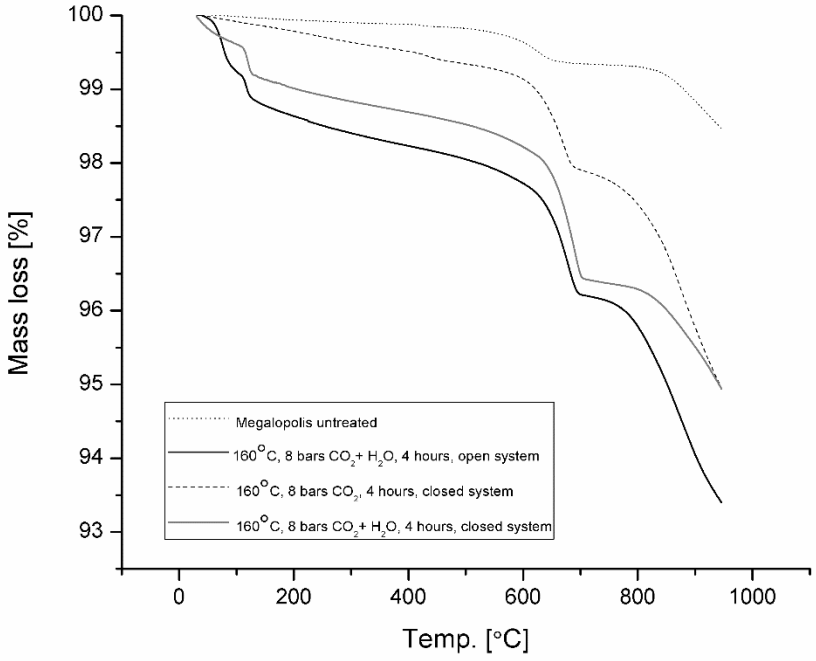


c)

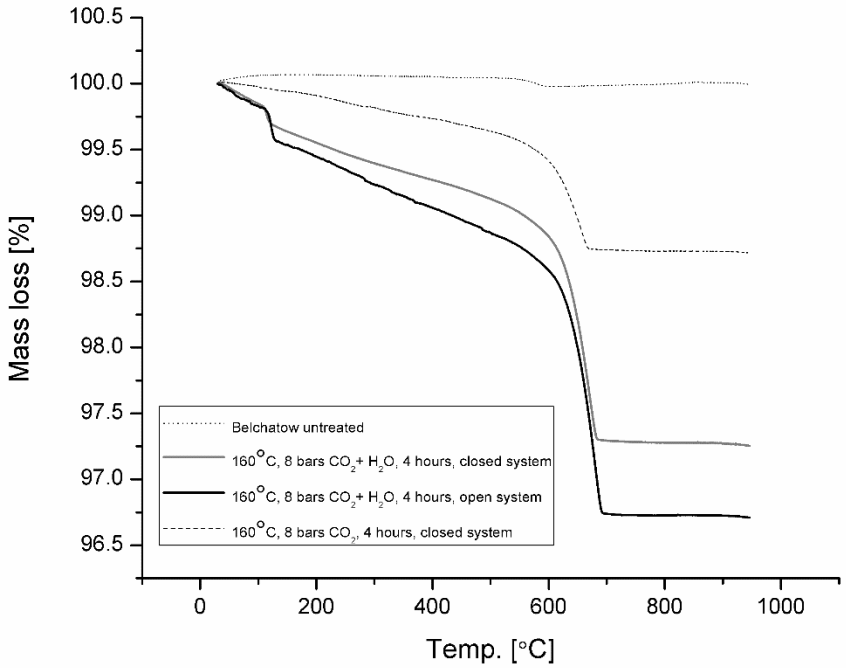
Figure 6. Results of TGA analysis for the treated samples: a) La Pereda fly ash, b) Megalopolis fly ash, c) Belchatow fly ash.


Mass loss [%]
Temp. [°C]
La Pereda untreated
160°C, 8 bars CO2+ H2O, 4 hours, open system
160°C, 8 bars CO2+ H2O, 4 hours, closed system
160°C, 8 bars CO2, 4 hours, closed system

a)

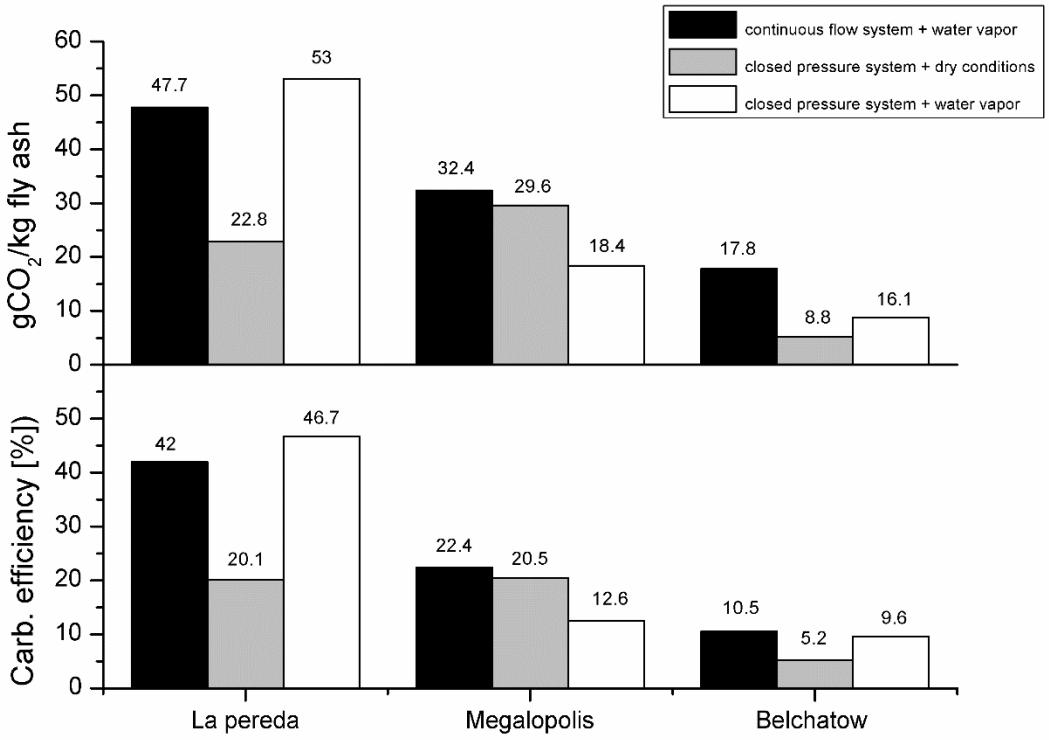

Mass loss [%]
Temp. [°C]
Megalopolis untreated
160°C, 8 bars CO2+ H2O, 4 hours, open system
160°C, 8 bars CO2, 4 hours, closed system
160°C, 8 bars CO2+ H2O, 4 hours, closed system

b)



c)

Figure 7. Calculated values of the sequestration capacity (g CO_2/kg fly ash) and carbonation efficiency (ζ_{Ca} [%]) of the samples.


continuous flow system + water vapor
closed pressure system + dry conditions
closed pressure system + water vapor
gCO2/kg fly ash
Carb. efficiency [%])
47.7
22.8
53
32.4
29.6
18.4
17.8
8.8
16.1
42
20.1
46.7
22.4
20.5
12.6
10.5
5.2
9.6
La pereda
Megalopolis
Belchatow